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The Instability of Ni\{N(SiMe\(_3\))\}_2: A Fifty Year Old Transition Metal Silylamide Mystery

Michelle Faust\(^*\), Aimee M. Bryan\(^†\), Akseli Mansikkamäki\(^‡\), Petra Vasko\(^‡\), Marilyn M. Olmstead\(^†\), Heikki M. Tuononen\(^*\),*, Fernande Grandjean\(^§\), Gary J. Long\(^§\), and Philip P. Power\(^†\)*

Dedicated to the memory of Prof. G. L Hillhouse, maker of many fine contributions to nickel chemistry.

Abstract: The characterization of the unstable Ni(II) bis(silylamide) Ni\{N(SiMe\(_3\))\}_2(1), its THF complex Ni\{N(SiMe\(_3\))\}_2(THF) (2), and the stable bis(pyridine) derivative trans-Ni(N(SiMe\(_3\))\_2(py)_2) (3), are described. Both 1 and 2 decompose at ca. 25 °C to a tetrameric Ni(I) species, [Ni(N(SiMe\(_3\))]_4 (4), also obtained from LiN(SiMe\(_3\)) and NiCl\(_2\)(DME). Experimental and computational data indicate that the instability of 1 is likely due to ease of reduction of Ni(II) to Ni(I) and the stabilization of 4 via London dispersion forces.

In the early 1960s, Bürger and Wannagat reported that the bis(trimethylsilyl)amido ligand -N(SiMe\(_3\)) stabilized the first 2- and 3-coordinate, open shell transition-metal complexes.\(^[1,2]\) These include the Ni(II) species Mn(N(SiMe\(_3\))\_2)\_2,\(^[2]\) Co(N(SiMe\(_3\))\_2)\_2,\(^[1,7]\) and Ni(N(SiMe\(_3\))\_2)\_2.\(^[2,23]\) The corresponding Fe(II) derivative, Fe(N(SiMe\(_3\))\_2), was described in 1988.\(^[3]\) Uniquely, the Ni(II) amide was reported to be unstable, decomposing to a black solid at room temperature.\(^[2]\) The Mn, Fe, and Co silylamides are thermally stable and have proven to be valuable synthons in diverse applications, especially striking because several other stable, homoleptic Mn, Fe, and Co analogs.\(^[23,25]\) Treatment of 1 or 2 with excess pyridine gave the diamagnetic bis(pyridine) complex trans-Ni(N(SiMe\(_3\))\_2(py)_2) (3) as gold crystals. Complex 3 is stable as a crystalline solid or in pyridine solution at 25 °C, but dissociation of pyridine ligands in NMR solvents results in rapid decomposition.

Scheme 1. Summary of the synthesis of Ni\{N(SiMe\(_3\))\}_2 (1) and its THF and pyridine complexes 2 and 3.

For the structures of 2 and 3 (Figure 1), 2 has essentially trigonal planar geometry at Ni (Σ \(= 359.86°\)) and it narrowly misses having a C\(_2\) axis along the Ni-O bond, like its Fe and Co analogs.\(^[12,23,24]\) The Ni-N (1.846(2) and 1.8570(4) Å) and Ni-O (2.0143(2) Å) bonds in 2 are shorter by ca. 0.05 and 0.02 Å than the Co-N and Co-O bonds in its Co analog (Table S2). However, the Ni-N bond lengths are similar to those in Ni(N(Mes)BMes\(_2\)) (avg. 1.865 Å).\(^[15,16]\) The bis(pyridine) complex 3 has nearly ideal square planar coordination at Ni with interligand angles near 90°. The Ni-N(THF) bond lengths (1.939(4) and 1.9449(4) Å) are longer than those in 2 by ca. 0.08 Å, which is likely due to the higher coordination number and increased steric crowding in 3. The Ni-N bonds are longer than those in Ni(N(Mes)BMes\(_2\)) (avg. 1.884 Å).\(^[16]\) Ni(N(SiMe\(_3\))Dipp\(_2\)) (1.8029(9) Å),\(^[21]\) (1.828 Å for terminal Ni-N bonds),\(^[14]\) and Ni(N(H)Ar)\(_2\) (Ar = terphenyl) (avg. 1.821 Å).\(^[17,18]\)

Figure 1. Thermal ellipsoid (50%) plots of Ni\{N(SiMe\(_3\))\}_2(THF) (2, left) and Ni\{N(SiMe\(_3\))\}_2(py)_2 (3, right). Selected bond lengths (Å) and angles (°) for 2: Ni1-N1 1.8646(2), Ni1-N2 1.8570(2), Ni1-N3 1.8464(2), Ni1-N4 1.8547(2), Ni1-N5 1.8570(2), Ni1-N6 1.8570(2), Ni1-N7 1.8464(2), Ni1-N8 1.8570(2).

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Ni1-O1 2.0143(2), N1-Ni1-N2 140.66(5), N1-Ni1-O1 109.42(19), 
N2-Ni1-O1 109.78(19); 3: Ni1-N1 1.9394(4), Ni1-N2 1.9449(4), 
Ni1-N3 1.9305(4), Ni1-N4 1.9314(4) Å, N1-Ni1-N2 179.2607(3), 
N3-Ni1-N4 179.0992(2).

Originally, Bürgel and Wannagat reported that blood red 
[Ni(N(SiMe3)2)2H]+ (probably [Ni(N(SiMe3)2)2Cl](THF)) turned black 
after a short time at room temperature. [2] We also found that 1 
and 2 became black within 30 minutes at ca. 25 °C, but had 
greater stability as hydrocarbon solutions, whose red colors 
persist for 2–3 days at ca. 25 °C. A sample of 1 in toluene 
decomposed over 4–5 weeks during which time the red solution 
became black and precipitated black crystals that were shown to 
be [Ni(N(SiMe3)2)2]4 (4) by X-ray crystallography. 1H NMR 
spectroscopy of 2 in CD6 indicated that decomposition to 4 
yielded a second product which is HN(SiMe3)2 based on the 
observed singlet at ca. 0.1 ppm (Figure S7). Compound 4 can 
also be synthesized from Li[N(SiMe3)2] and NiC6(DME) in Et2O.[25] 
Workup of the dark amber solution afforded black crystals of 
4 suitable for X-ray crystallography.

The structure of 4 (Figure 2) has four Ni(I) ions in an 
approximate square plane and bridged by four -N(SiMe3)2 
ligands. A Cc axis bisects the N(1) and N(3) atoms, to give two 
crystallographically unique Ni(1) sites on adjacent edges of the 
Ni4 square. The Ni-Ni units deviate from linearity such that the 
Ni nuclei are displaced toward each other with Ni−Ni distances 
of 2.4328(4) and 2.4347(5) Å (cf. sum of single bond covalent 
radii for two Ni atoms = 2.20 Å).[27] The Ni−Ni distances in 4 are 
ca. 0.25 Å shorter than the Cu−Cu separations in 
[Cu2(N(SiMe3)2)2]2+.[25,28] 2.6770(7) and 2.6937(7) Å. Consistent 
with its bridging character, the average Ni-N bond length in 4 
(1.916 Å) is longer than those in two-coordinate Ni(II) amides 
(1.803(9)−1.885(4) Å)[15,18–20] and in the three-coordinate Ni(I) 
amides (Ph2P)2Ni[N(SiMe3)2] (1.88(1) Å)[29] 
[(CHN(Dipp))2C]Ni[N(SiMe3)2] (1.865(2) Å)[30] and 
(Bu3PCH2CH2PBu3)Ni(N(H)Dipp) (1.882(2) Å).[31]
The energy difference comes from the M(II) oxidation potentials of the related amido M(I) monomers [M(N(SiMe$_3$)$_3$)$_2$Dipp]$_2$ \(-0.152\) and \(-1.082\) V for Co and Ni, respectively,[39] which indicate that with amido ligands the process Ni(II) \(\rightarrow\) Ni(I) is more favored than Co(II) \(\rightarrow\) Co(I).

Indirect evidence for homolytic Ni-N dissociation comes from the reaction of Na[N(SiMe$_3$)$_3$] and NiI in pyridine which yielded an orange solution. Workup gave two crystalline products: orange blocks of Ni[N(SiMe$_3$)$_3$][Ni(SiMe$_3$)$_3$CH$_3$]$_2$(py)$_3$ (5) and gold needles of the aforementioned 3 in a ca. 3:1 ratio. In 5 (Figure 4), Ni is bound to two cis-oriented pyridines, an amido nitrogen (N1), and the carbon from a deprotonated Si2 methyl group. The C-H activation of methyl substituents in sterically crowded trimethylsilylamido transition metal complexes is well-known,[21,34-38] but 5 is apparently the first example for nickel. Complex 5 has distorted square planar geometry at Ni (\(\Sigma^*\) Ni = 360.07°) and a lengthening of the Ni-py bond trans to the deprotonated methyl group, Ni1-N2 = 1.9992(15) Å (avg. 1.883 Å). Another interesting feature of 5 is its slightly pyramidal geometry at N1 (\(\Sigma^*\) N1 = 353.74°), whereas 2 and 3 have planar geometry at the amido nitrogens.

In conclusion, we have described the unstable Ni(II) bis-

Figure 4. Thermal ellipsoid (50%) drawing of Ni[N(SiMe$_3$)$_3$][Ni(SiMe$_3$)$_3$]$_2$(py)$_3$ (5). Ni1-N1 1.9197(14) Å, Ni1-N2 1.9992(15) Å, Ni1-N5 1.9119(15) Å, Ni1-C6 1.9707(17) Å, Si2-C6 1.8329(17) Å, N2-Ni-N3 87.51(6)°, N3-Ni-C6 89.72(6)°, C6-Ni1-N1 84.41(6)°, N1-Ni1-N2 98.42(6)°.

In conclusion, we have described the unstable Ni(II) bis-

References